

IS RHT ALIVE AND LIVING IN VENEZUELA?

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INTRODUCTION

Under coal liquefaction conditions, hydrogen transfer reactions of various types are so facile, and coal structures so varied and unknown, that were it not for model compounds, the concept of "hydrogen transfer" in coal liquefaction would be little more than a mantra which we recite. Several years ago, studies of hydrogen-transfer reactions in model compounds led to the suggestion, if not the rigorous proof, that a "missing link" in the system of known H-atom transfer reactions was not only kinetically accessible under liquefaction conditions, but also played a key role in bond cleavage during liquefaction.(1-4) More recently, however, specific model-compound and computational studies (5-7) have led researchers to question the general accessibility of "radical hydrogen-transfer" (RHT) compared to other H-transfer pathways. In light of this recent work, it is important to articulate more clearly the limited "window of opportunity" originally posited (2) for RHT, and to reconsider some other model compound systems in each of which one or more of the various alternative transfer pathways are themselves insufficient to account for the observed reaction. The particular difficulty embodied in the following discussion is that no single system has yet been identified in which RHT can be claimed to be free of competition with *all* other H-transfer routes. The ultimate goal of this reconsideration of model compound studies is to obtain an improved view of the probable importance of RHT in coal liquefaction and in catalytic hydrotreatment of heavy oils.

There are two aspects of hydrogen transfer as related to fossil fuel conversion: what hydrogen transfer accomplishes, and how the transfer takes place. In recent years there has been an evolution of thinking related to both aspects. H-transfer was once considered to come only after weak-bond homolysis, serving merely to prevent retrogressive reactions of fragment radicals. In recent years, however, many model compound studies (1,2,4,8-10) have shown beyond a doubt that H-atom transfer, both abstractive and additive, and not involving free H-atoms, induces the cleavage of strong bonds in coal-related structures under the conditions of coal liquefaction. However, the precise modes by which the additive H-transfer occur under any specific conditions have been very difficult to determine with any certainty. It is this latter aspect that we primarily address in this paper.

EXPERIMENTAL SECTION

This paper relies primarily on thermochemical data from the literature and on published model compound kinetic studies, including those of the authors. In most cases, the experimental techniques have involved batch reaction at 350-400°C in borosilicate or fused-silica ampoules housed in a pressure vessel, or in small stainless steel micro-reactors.(2-4) Analyses were generally performed by GC-FID and GC-MS.

RESULTS AND DISCUSSION

Trends in RHT competitiveness with Shifts in Thermochemistry. As reiterated recently (7), it has been asked repeatedly over the last 50 years (2,3,6,11,12) whether direct bimolecular transfer of a hydrogen atom from a hydrocarbon radical to an unsaturated system (RHT) might occur directly. That is, might a direct bimolecular reaction, occurring without the intervention of a free H-atom, be competitive under some conditions with the well-established sequence of H-atom elimination, followed by a separate step in which the H-atom adds to the unsaturated reactant? The answer to that limited question is probably yes. However, because RHT has to compete not only with sequential elimination and addition of H-atoms, but also with H-transfer from closed-shell H-atom sources (e.g., reverse radical-disproportionation, or RRD from hydroaromatic donor molecules themselves), there is likely a substantial range of structures and conditions for which RHT cannot easily be competitive. Notwithstanding difficulty of experimentally determining the precise contribution of RHT when the competitive reactions produce an identical set of products, the thermochemical requirements for a competitive RHT process can be easily delineated.

We will discuss these criteria starting with the anthracene-dihydroanthracene system, since it was the principal solvent used by us in the presentation of the case for RHT, and because Stein and coworkers (13) have used it as both the solvent system and the reaction substrate in studying the kinetics of the net process shown in Reaction 1 (An* in Reaction 1 below is simply anthracene, labeled with an ethyl group at the relatively unreactive 2-position).

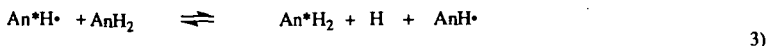


1)

In this case, the reverse radical-disproportionation we have posited as a common initiation step for RHT (often rapid enough to be a pre-equilibrium) simply becomes the stoichiometric transfer step.



The overall process is completed by H-abstraction (Reaction 3).



First, it should be stressed that the system in Reaction 1 is not really a good case for RHT, as becomes clear when the component steps are examined. As we have already noted, in the system studied by Stein (13), RRD is the stoichiometric transfer step; by the time that RHT potentially appears on the scene, the net H-transfer has already been accomplished. Obviously, the only possibility for RHT to play a substantial role in the production of An^*H_2 would be in the limit where the labeled acceptor was in a substantial minority, with respect to an unlabeled acceptor or solvent.

Even in the case where the dominant acceptor is not the substrate to be cleaved, one may ask the intuitively appropriate question, "Why would it be favorable, if the original source of hydrogen in any case is to be AnH_2 , to shuttle the hydrogen through the carrier radical AnH^* , when this does not in any way change the overall ΔH° ?" This question is posed schematically in Figure 1. The answer to the question is (a) in coal liquefaction, an entire assembly of acceptor species, polycyclic Ar, are likely to be present in the solvent at high concentration, and may be statistically (and perhaps thermochemically) favored as the first acceptor of hydroaromatic donor hydrogen, and (b) the stoichiometry of AnH^* production by RRD means that two molecules of the carrier radical AnH^* are produced in each RRD step, so that the steady state concentration of ArH^* varies exponentially with $1/2 \Delta H^\circ_{\text{RRD}}$ (i.e., the thermodynamic "cost" of producing ArH^* is only one-half that of producing two ArH^*). This is illustrated in Figure 1 by the hypothetical potential energy diagram where anthracene, dihydroanthracene, and dinaphthylmethane are representatives of the generalized system of aromatic/hydroaromatic solvent system (Ar/ArH_2) and cleavable acceptor $\text{Ar}'\text{-X}$.



$$\frac{\text{Rate}_{\text{RRD}}}{\text{Rate}_{\text{RHT}}} = \frac{k_{\text{RRD}} [\text{ArH}_2] [\text{Ar}'\text{-X}]}{k_{\text{RHT}} [\text{ArH}^*] [\text{Ar}'\text{-X}]} = \frac{k_{\text{RRD}} [\text{ArH}_2]}{k_{\text{RHT}} (K_4 [\text{ArH}_2] [\text{Ar}])^{1/2}}$$

$$\frac{A_{\text{RRD}} (e^{-E_{\text{RRD}}/RT}) [\text{ArH}_2]}{A_{\text{RHT}} e^{-E_{\text{RHT}}/RT} ([e^{\Delta S^\circ_{\text{R}}/R} e^{-\Delta H^\circ_{\text{RRD}}/RT}] [\text{ArH}_2] [\text{Ar}])^{1/2}}$$

For $[\text{Ar}] = [\text{ArH}_2]$, $\Delta S^\circ_{\text{RRD}} = 0$, $E_{\text{RRD}} = \Delta H^\circ_{\text{RRD}}$, $A_{\text{RRD}} = A_{\text{RHT}}$, and where Ar and $\text{Ar}'\text{-X}$ are equally good H-acceptors, at equal concentrations, this becomes:

$$\frac{\text{Rate}_{\text{RRD}}}{\text{Rate}_{\text{RHT}}} = \frac{e^{-\Delta H^\circ_{\text{RRD}}/RT}}{e^{-(E_{\text{RHT}} + \frac{1}{2} \Delta H^\circ_{\text{RRD}})/RT}}$$

Thus, when Ar and $\text{Ar}'\text{-X}$ are equally good acceptors, reaction via RHT ArH^* (Reaction 6) will tend to be preferred to the extent that the activation energy for the thermoneutral RHT is $< 1/2 \Delta H^\circ_{\text{RRD}}$. One-half of $\Delta H^\circ_{\text{RRD}}$ is 17 kcal/mol in the anthracene system; all other kinetic factors being equivalent, an activation energy for RHT of less than 17 kcal/mol or a concentration of Ar greater than that of ArH_2 will favor transfer via RHT, rather than directly from ArH_2 to $\text{Ar}'\text{-X}$.

As it happens, our original fitting of data for dinaphthylmethane cleavage in anthracene/dihydroanthracene (14) resulted in an activation energy for thermoneutral RHT of

16.5 kcal/mol, that is, putting RHT in the $\text{An}/\text{AnH}_2/\text{Ar}'\text{-X}$ system only at the threshold of RHT feasibility. However, as the H-accepting thermochemistry of the substrate $\text{Ar}'\text{-X}$ moves away from being thermoneutral, the RHT process can become more accessible, depending on whether its major competition is from RRD or free H-atom addition.

If, as will commonly be the case with an anthracene/dihydroanthracene solvent system, RRD is the major competitor to an (actual or potential) RHT, then a shift in the substrate (or solvent) thermochemistry so as to make the substrate to be a relatively *poorer* acceptor, raising the ΔH° for both RRD and RHT, will make RHT relatively more favorable. While this may seem counter-intuitive, it results because on the one hand, the increase in $\Delta H^\circ_{\text{RRD}}$ leads to an exactly equal increase in E_{RRD} (as a reaction with zero intrinsic activation energy, i.e., essentially no activation energy in the reverse direction, there can be no further lowering of the intrinsic activation energy). On the other hand, the activation energy for RHT will increase, in the terms of the Evans-Polanyi formalism, by only a fraction of the increase in $\Delta H^\circ_{\text{RHT}}$ (the fraction being given by $1-\alpha$, where α is the Evans-Polanyi factor describing the fraction of a change in the thermodynamics ($\Delta\Delta G^\circ$) of an exothermic reaction that is applied to the kinetics (E_a) of the reaction). Thus an increase in $\Delta H^\circ_{\text{RHT}}$ from 0 to roughly +13 kcal/mol as the substrate $\text{Ar}'\text{-X}$ in an anthracene/dihydroanthracene solvent system goes from an H^\bullet acceptor that is equally as good as anthracene to one that is 13 kcal/mol poorer (e.g., naphthalene) (14), will result in an increase of 13 kcal/mol in E_{RRD} , but in an expected increase of only roughly 50 to 70% of this value, or 6 to 9 kcal/mol, in E_{RHT} . At 400°C, this will result in a shift toward RHT, relative to RRD, by a factor of 20 to 200. Thus the thermochemistry predicts that RHT will be relatively more favored, in anthracene, by an $\text{Ar}'\text{-X}$ that is a *poorer* acceptor than anthracene.

In contrast to the case for competition with RRD, if the major competition for an RHT process is sequential elimination and addition of a free H atom, then change in the substrate (or solvent) so as to make RHT more *exothermic* will be a relative benefit to RHT. This is a more easily intuited result than that discussed above: if the solvent system is one in which the carrier radical ArH^\bullet eliminates an H atom fairly readily (e.g., phenanthrene/dihydrophenanthrene), then making the substrate $\text{Ar}'\text{-X}$ a better acceptor, so that the RHT is exothermic, will obviously not influence the unimolecular H-elimination, but will facilitate the RHT step by $\alpha(\Delta\Delta H^\circ_{\text{RHT}})$, or 30 to 50% of the $\Delta\Delta H^\circ_{\text{RHT}}$. In the case of moving from a phenanthrene-like to an anthracene-like acceptor, this will result, at 400°C, in a shift toward RHT *relative* to free H-atom transfer, by a factor of 10 to 40.

The above considerations reiterate that we expect the contribution of RHT to be sandwiched in a limited region between dominance by RRD on the one hand, and dominance by free H-atoms on the other. More specifically, they indicate that the thermoneutral-RHT system, anthracene/dihydroanthracene/anthracene-X, investigated by Stein (13) is, as he indicated, not the best system for observing RHT, whereas the anthracene/dihydroanthracene/naphthalene-X in which we claimed to have observed RHT (2,14), is relatively much better for this purpose. The exothermic-RHT system, phenanthrene/dihydrophenanthrene/anthracene-X, where Stein did claim (3) to observe substantial RHT, is a relatively good system for that purpose, much better than the near-thermoneutral-RHT system, phenanthrene/dihydrophenanthrene/naphthalene-X, where our data fitting (14) suggested transfer by free H-atoms was twice as important as RHT, even at an aromatic/hydroaromatic ratio of 2/1.

H-Transfer Efficiency and Selectivity. In those of the above cases where the cleavage of dinaphthylmethane was involved, the task of determining the dominant pathway was often made more difficult by competition from indirect cleavage pathways involving initial H-transfer to a non-ipso position on $\text{Ar}'\text{-X}$, followed by additional H-transfers to generate reduced, uncleaved products. These uncleaved products can then undergo cleavage either by homolysis of bonds that have been made doubly benzylic by the partial reduction, or by H-abstraction to produce the initially desired, easily fragmentable ipso-radical. In the case of our studies on the anthracene/dihydroanthracene/dinaphthylmethane system, we attempted to limit this additional difficulty by focusing on reaction conditions that minimized multiple H-transfers, i.e., high ratios of anthracene/dihydroanthracene. The high aromatic/hydroaromatic ratio increases H-transfer efficiency by limiting the chances that an initial hydrogen transfer to a non-ipso position (by whatever transfer mechanism) would be followed by additional transfers so as to result in a reduced-uncleaved product. This observed increase in efficiency under conditions of high PAH content, which has been previously discussed (10,14), is strikingly parallel to observed shifts in efficiency in both liquefaction (16) and gasification. (17)

The additional route to cleavage through multiple-H-atom reduction that is discussed in the previous paragraph has made it somewhat difficult to unambiguously apply the otherwise very definitive selectivity diagnostic for the active H-transfer agent. Nevertheless, we believe that positional selectivity in H-atom transfer is a least arguably a useful indicator. Free H-atoms are highly reactive and are expected, and found (14), to show relatively little positional preference for attack at the electronically favored 1-position of naphthalene, as compared to the slightly less favored 2-position. Thus, dominant free H-atom-induced cleavage of 1,2-dinaphthylmethane approaches a 2-methylnaphthalene/1-methylnaphthalene ratio of about 1.6. (14) Any increase from this ratio necessarily represents a contribution from some other, more selective, H-transfer agent. Cleavage in the anthracene/dihydroanthracene system is found (14) to be highly selective, with the above ratio reaching a value of about 6. However, both RHT

and RRD are expected to be very selective, and so this high value, by itself, does not constitute evidence for RHT. In dihydrophenanthrene, however, where RRD is ruled out as a stoichiometric H-transfer step (and where free H-atoms are the main RHT competitor), the observed ratios are 3.0 to 3.5, still substantially higher than 1.6. The higher selectivity ratio would be unequivocal evidence for RHT contribution, were it not for the fact that, even at fairly high phenanthrene/dihydrophenanthrene ratios, there is still a substantial amount of product derived from reduction followed by cleavage.

In the pyrene/dihydropyrene system, the observed selectivity appears still more suggestive, even if not fully unambiguous. Since cleavage rates are about two times higher than in the anthracene solvent system under comparable conditions, and the C-H bond strength in dihydropyrene is 5 kcal/mol *higher* than in dihydroanthracene (14), transfer by RRD is completely ruled out as the cleavage-inducing step. On the other hand, the 2-methylnaphthalene/1-methylnaphthalene selectivity ratio is about 4, well above the 1.6 expected for free H-atoms.(2) The obvious conclusion is that H transfer by RHT is substantial in the case of pyrene; however, here too, the result remains somewhat tainted by the contribution of pathways that involve reduction followed by cleavage.

1,2-Dihydronaphthalene Disproportionation. As is well appreciated by those who have attempted to use either simple product identification or kinetic modeling of total rates, determination by these means of the precise portion of reaction that is accounted for by RHT tends to be very difficult. The best chance for distinction usually lies with an internal comparison and its shift as concentrations change, such as in simple dilution. One of the earliest cases of this approach was that of 1,2-dihydronaphthalene (DHN) disproportionation.(1) The radical-chain disproportionation of 1,2-dihydronaphthalene gives equal amounts of tetralin and naphthalene. The propagation steps, as shown in Scheme 1, are abstraction of a hydrogen from the 3-position of DHN by tetralyl radical (T^{\bullet}), followed by either an RHT to transfer a hydrogen from the 1-hydronaphthyl (NH^{\bullet}) radical to DHN, or sequential H-atom elimination from NH^{\bullet} and addition to DHN, to accomplish the same net change.

The sole difference between these disproportionation pathways involving either free H-atoms or RHT stems from the fact that free H atoms can not only add to DHN, but also abstract from DHN to form H_2 . RHT cannot produce H_2 . In the case of H-abstraction by H^{\bullet} , the net products of DHN self-reaction become naphthalene and H_2 , rather than naphthalene and tetralin. Since the H-transfer by RHT with which the elimination-addition sequence may be competing is a bimolecular reaction, its rate will be decreased by dilution, whereas that for the unimolecular elimination will be unaffected. The subsequent addition of, and abstraction by, H atoms are bimolecular reactions that will be slowed by dilution, but since they both involve reactions with the same molecule, namely DHN (Reactions 7a and 7b in Scheme X), their ratio will not shift with dilution. Thus, the only change with dilution will be the competition between RHT (Reaction 4) and H-atom elimination (Reaction 6). Increasing dilution will increase the relative chance of H-atom elimination, and, to the extent that abstraction by H^{\bullet} competes with addition of H^{\bullet} , the parasitic production of H_2 and naphthalene production without tetralin production will increase.

The quantitative expectations from a steady-state analysis of this system are shown in Figure 2 (reprinted from reference 1), as a series of calculated lines, each of which is based on a particular value of the fraction of free H^{\bullet} that add to (rather than abstract from) DHN. If the reactions in Scheme 1 correctly describe the disproportionation, then the data should be fitable to one of the curves in Figure 2 simply by adjustment of the k_4/k_6 ratio.

Although the naphthalene-tetralin ratios did not vary widely for a substantial range of dilutions, the data are not scattered, and they fit the function form very well, so as to leave little room for adjustment. The very existence of a curved data plot in Figure 2 is significant: if there is no H-transfer by RHT, there will be no competition for the chain propagation by free H-atoms, and there can be no shift in the naphthalene/tetralin ratios with dilution. In fact, these measurements were prompted by related data of Allen and Gavalas (18), and of Franz and coworkers (19), which indicated shifting H_2 yields with changes in dilution. Thus, the observation of *any* shift in the naphthalene/tetralin ratio is evidence for a competing RHT reaction. This conclusion is unequivocal, *if* (a) the chain length is long and the reverse of the initiation step (a bimolecular reaction) is not a significant product generator, and (b) other side reactions do not distort the product ratio. Both of these qualifications were considered in our original publication and judged to be unimportant.(1) Nevertheless, given the apparently unequivocal nature of the evidence for RHT from this earlier dilution study, and current questions about the accessibility and generality of RHT, we believe the case of 1,2-dihydronaphthalene disproportionation should be re-examined.

SUMMARY

Re-examination of the trends in competition between RHT, RRD, and free H-atom elimination/addition that one expects from thermochemical consideration, reiterates that the supposed case of RHT that has been most called into question by recent studies (7), is in fact expected to be among the poorest of all specific examples of RHT yet claimed. Specific cases of either exothermic or endothermic RHT (e.g., phenanthrene/dihydrophenanthrene, anthracene, or

anthracene/dihydroanthracene/dinaphthylmethane, or pyrene/dihdropyrene/dinaphthylmethane are all more expected and more credible. Reexamination of the original 1,2-dihydronaphthalene disproportionation data continues to make this case appear a very credible example of RHT. Nevertheless, the framework of thermochemical considerations discussed here again makes it clear that there is a limited window of opportunity for RHT, in between RRD on the one hand and free H-atom elimination/addition on the other. Current attention would be most usefully directed to this window.

In any event, the case of shifting hydrogen-utilization efficiencies illustrates the important point that competing and shifting competition between various transfer pathways does not render consideration of them irrelevant. On the contrary, the shifting competition makes for situations in which liquefaction effectiveness can vary substantially with shifts in solvent composition or temperature. The situation is indeed complex, and model compounds, judiciously chosen and interpreted in light of data with actual coals or heavy oils, represent the only feasible route for us mortals into the labyrinth of fossil fuel chemistry.

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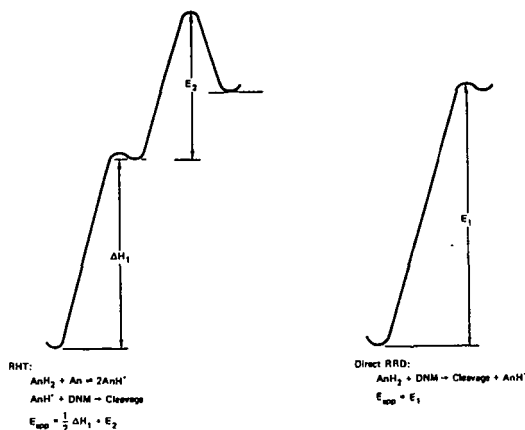
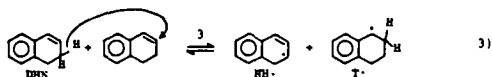
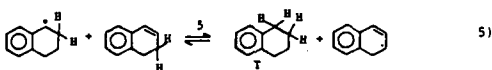
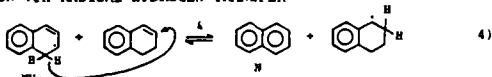


Figure 1. Illustrative potential energy diagram for direct- (RRD) and carrier-radical-mediated hydrogen-transfer (RHT) in the anthracene/9,10-dihydroanthracene/1,2-dinaphthylmethane system.

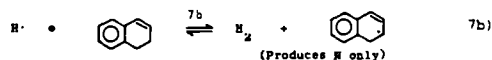
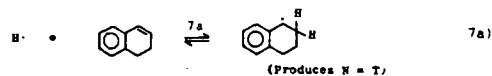
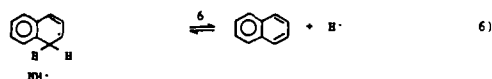
INITIATION/TERMINATION



PROPAGATION VIA RADICAL-HYDROGEN-TRANSFER



PROPAGATION VIA FREE H \cdot



Scheme 1. Radical-chain reaction sequence for 1,2-dihydronaphthalene disproportionation.

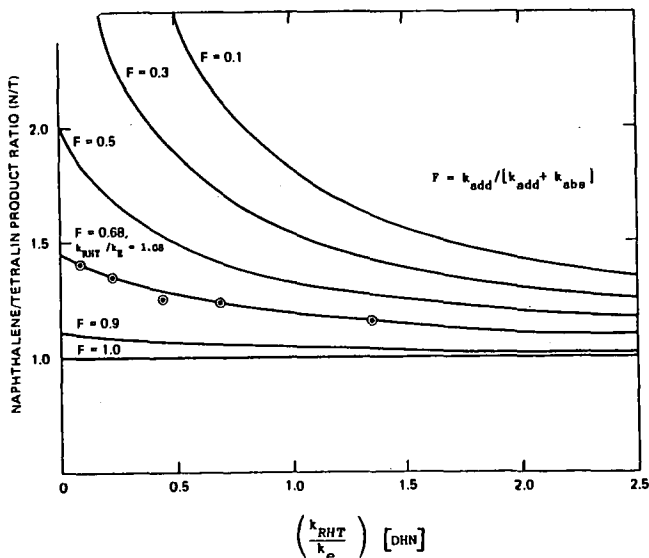


Figure 2. Observed and calculated effect of dilution with biphenyl on the naphthalene/tetralin product ratio in the disproportionation of 1,2-dihydronaphthalene at 385°C.